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(54) CATALYST FOR OLEFIN POLYMERIZATION AND PROCESS FOR PREPARING OLEFIN POLYMER BY USING THE SAME.

(57) A novel catalyst which catalyzes homopolymerization of an olefin having 2 or more carbon atoms or copolymerization of two or more olefins, and a process for preparing olefin polymers by using it. High-molecular olefin polymers can be produced in high yields by polymerizing or copolymerizing an olefin by using a catalyst system composed of a transition metal compound of $M(R)(OR')_mX_{n-(l+m)}$ and aluminooxane or a catalyst system composed of a transition metal compound of $M(R)(OR')_mX_{n-(l+m)}$, aluminooxane, and an organic compound having at least two hydroxy groups.

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CATALYST FOR OLEFIN POLYMERIZATION AND
PROCESS FOR PRODUCING OLEFIN POLYMER USING THE CATALYST

1 Technical Field

The present invention relates to a catalyst for olefin polymerization (homopolymerization of an olefin of 2 or more carbon atoms or copolymerization of
5 two or more olefins of 2 or more carbon atoms), as well as to a process for producing an olefin polymer using said catalyst. More particularly, the present invention relates to a catalyst system comprising a transition metal compound having a particular structure and a
10 aluminoxane, as well as to a process for producing a high molecular olefin polymer at a high efficiency by using said catalyst system.

Background Art

Conventional processes for producing olefin
15 polymers generally employ a catalyst system consisting of a solid titanium compound (composed mainly of titanium trichloride) and an organoaluminum compound, or a catalyst system comprising a solid which is titanium tetrachloride supported on magnesium chloride, an
20 organoaluminum compound and an electron-donating compound. Also, there is proposed a process using a polymerization catalyst consisting of a cyclopentadienyl compound of

1 titanium, zirconium or hafnium and an aluminoxane [e.g.
Japanese Patent Application Kokai (Laid-Open) No.
19309/1983 (USP No. 4,542,199), Japanese Patent Application
Kokai (Laid-Open) No. 217209/1985]. These processes
5 using said polymerization catalysts are defective in
that the olefin polymers, particularly, the propylene
polymer obtained has a small molecular weight.

Meanwhile, a process for producing olefin
polymers is proposed which uses, as part of the catalyst
10 components, $Ti(OR)_nX_{4-n}$ and an aromatic hydrocarbon
compound having at least 1 hydroxyl group (USP No.
4,525,556). The catalyst system used in this process,
however, further requires, as other essential catalyst
components, MgR_2 and an inorganic or organic halogen
15 compound and furthermore requires, as an organoaluminum
compound, AlR_nX_{3-n} , (wherein R is a hydrocarbon group, X
is halogen, n and n' are each a value of 0 to 3 and
 $n+n'=3$).

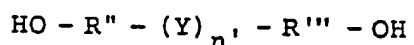
Disclosure of the Invention

20 The object of the present invention is to solve
the above mentioned problems and to provide a process
for producing a high molecular olefin polymer with a
high efficiency by using a novel catalyst system.

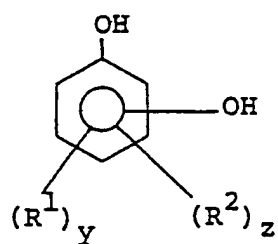
The present invention relates to

25 (1) a catalyst for olefin polymerization comprising:
a catalyst component (A) which is a transition
metal compound represented by the general formula

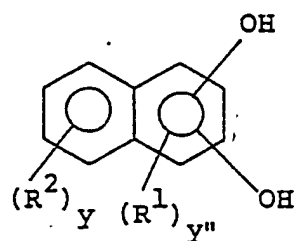
- 1 $M(R)_l(OR')_mX_{n-(l+m)}$ (wherein M represents a transition metal atom; R and R' each represents a hydrocarbon group of 1 to 20 carbon atoms; X represents a halogen atom; l, m and n represent numbers satisfying $l \geq 0$, $m > 0$
- 5 and $n-(l+m) \geq 0$; and n corresponds to the valency of the transition metal), and
- a catalyst component (B) which is an aluminoxane obtained by the reaction of a trialkylaluminum and water, and
- 10 (2) a catalyst for olefin polymerization comprising:
- a catalyst component (A) which is a transition metal compound represented by the general formula
- $M(R)_l(OR')_mX_{n-(l+m)}$ (wherein M represents a transition metal atom; R and R' each represents a hydrocarbon group
- 15 of 1 to 20 carbon atoms; X represents a halogen atom; l, m and n represent numbers satisfying $l \geq 0$, $m \geq 0$ and $n-(l+m) \geq 0$; and n corresponds to the valency of the transition metal),
- a catalyst component (B) which is an aluminoxane
- 20 obtained by the reaction of a trialkylaluminum and water, and
- a catalyst component (C) which is an organic compound having at least 2 hydroxyl groups, represented by the general formula (I), (II), (III), (IV), (V) or
- 25 (VI)



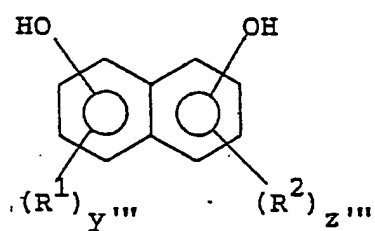
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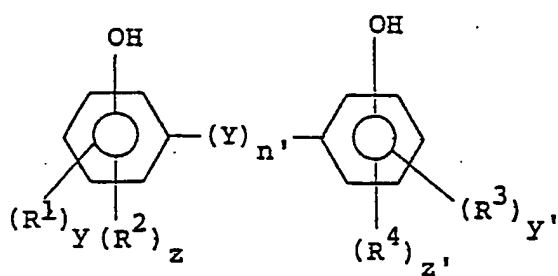
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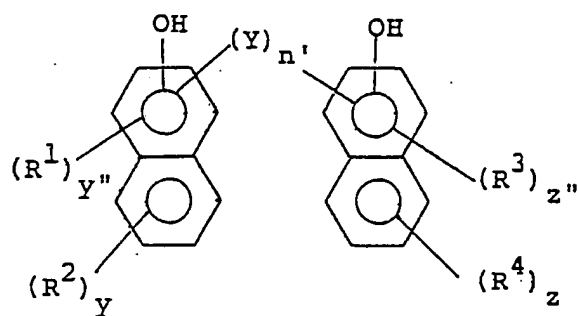
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(IV)



(V)



(VI)

- 1 [wherein R" and R''' each represents a hydrocarbon group of 1 to 20 carbon atoms; Y represents a hydrocarbon

group of 1 to 20 carbon atoms, -O-, -S-, -S-S-, -S-, $\begin{array}{c} \text{O} \\ \parallel \\ -\text{S}- \\ \parallel \\ \text{O} \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ -\text{S}- \\ \parallel \\ \text{O} \end{array}$,

-C-, $\begin{array}{c} \text{O} \\ \parallel \\ -\text{N}- \\ | \\ \text{R}^5 \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ -\text{P}- \\ | \\ \text{R}^5 \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ -\text{P}- \\ | \\ \text{R}^5 \end{array}$ or $\begin{array}{c} \text{R}^5 \\ | \\ -\text{Si}- \\ | \\ \text{R}^5 \end{array}$ (wherein R⁵ represents

- 5 hydrogen or a hydrocarbon group of 1 to 6 carbon atoms); R¹, R², R³ and R⁴ each represents a hydrocarbon group of 1 to 20 carbon atoms, a hydroxyl group, a nitro group, a nitrile group, a hydrocarbyloxy group or a halogen atom, and R¹, R², R³ and R⁴ may be same or different;
- 10 n' is 0 or an integer of 1 or larger and represents the times of repetition of the unit Y; y, y', y'', Y''', z, z', z'' and z''' each represents the number of a substituent bonding to an aromatic ring, y, y', z and z' each represents 0 or an integer of 1 to 4, y'' and z'' each
- 15 represents 0 or an integer of 1 to 2, and Y''' and z''' each represents 0 or an integer of 1 to 3], as well as to a process for producing an olefin polymer, characterized by homopolymerizing an olefin of 2 or more carbon atoms or copolymerizing two or more olefins of 2
- 20 or more carbon atoms by using the catalyst system (1) or (2).

Best Mode for Carrying Out the Invention

The present invention will be explained in

1 detail below.

In the transition metal compound represented by the general formula $M(R)_l(OR')_mX_{n-(l+m)}$ which is used as the catalyst component (A) in the present invention, specific examples of M include titanium, zirconium, hafnium, vanadium, etc. Of these, titanium and zirconium, in particular, give preferable results.

R and R' are each a hydrocarbon group of 1 to 20 carbon atoms. Of these, alkyl groups of 2 to 18 carbon atoms and aryl groups of 6 to 18 carbon atoms can be used preferably.

As specific examples of R and R', there can be mentioned alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, n-amyl, isoamyl, n-hexyl, n-heptyl, n-octyl, n-decyl, n-dodecyl and the like; aryl groups such as phenyl, naphthyl and the like; cycloalkyl groups such as cyclohexyl, cyclopentyl and the like; allyl groups such as propenyl and the like; aralkyl groups such as benzyl and the like; and so forth.

Of these, groups such as methyl, ethyl, phenyl, benzyl and the like are preferably used as R. As R', alkyl groups such as n-propyl, isopropyl, n-butyl, t-butyl and the like, as well as aryl groups such as phenyl and the like can be used preferably.

As examples of the halogen atom represented by X, there can be mentioned chlorine, bromine and iodine. Chlorine, in particular, can be used preferably.

1 l , m and n are numbers satisfying $l \geq 0$, $m > 0$
 and $n-(l+m) \geq 0$, in the catalyst system (1).

 Meanwhile, l , m and n are numbers satisfying
 $l \geq 0$, $m \geq 0$ and $n-(l+m) \geq 0$, in the catalyst system

5 (2). Therefore, a compound of $m=0$, for example, titanium
 tetrachloride or zirconium tetrachloride can be used as
 the catalyst component (A), in the catalyst system (2)
 comprising the catalyst component (A) which is a
 transition metal compound, the catalyst component (B)
 10 which is an aluminoxane and the catalyst component (C)
 which is an organic compound having at least 2 hydroxyl
 groups. Meanwhile, in the catalyst system (1) consisting
 of the catalyst component (A) and the catalyst component
 (B), the presence of hydrocarbyloxy group is essential.

15 As specific examples of the catalyst component
 (A), there can be mentioned titanium tetrachloride,
 zirconium tetrachloride, tetraisopropoxytitanium, tetra-
 n-butoxytitanium, tetra-*t*-butoxytitanium, diphenoxy-
 titanium dichloride, dinaphthaoxytitanium dichloride,
 20 tetraiospropoxyzirconium, tetra-*n*-butoxyzirconium, tetra-
t-butoxyzirconium, etc.

 The aluminoxane which is the catalyst component
 (B) is a polymer of an aluminum compound and is a linear
 compound represented by the general formula $R^a[Al(R^a)O]_n-$
 25 AlR^a_2 and/or a cyclic compound represented by the general
 formula $[Al(R^a)O]_{n+1}$. In these formulas, R^a is an alkyl
 group of 1 to 10 carbon atoms such as methyl, ethyl,
 propyl, butyl, pentyl or the like. Particularly, methyl

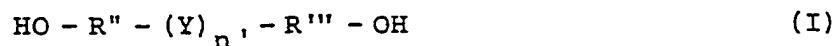
1 and ethyl groups are preferable. n is an integer of 1
or larger. Particularly, 1 to 20 are preferable.

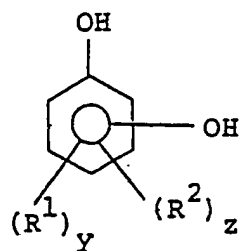
The aluminoxane can be obtained according to
various ordinary methods. In one method, it can be
5 synthesized by contacting a trialkylaluminum dissolved
in an appropriate hydrocarbon solvent, with water. In
this case, it is preferable that water be contacted
with an aluminum compound in a mild condition. There
are other methods such as a method of contacting steam
10 with an aluminum compound solution and a method of
slowly dropping a water-saturated organic solvent to an
aluminum compound solution. Also, there is a method
wherein copper sulfate hydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) or aluminum
sulfate hydrate [$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$] is reacted with an
15 aluminum compound.

When an aluminoxane is synthesized from
trimethylaluminum and water, it is common that a
linear compound and a cyclic compound are obtained
together.

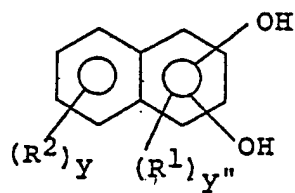
20 With respect to the mole ratio of the raw
materials of the aluminoxane, it is preferable that the
aluminum compound and water be used in equal moles.

In the compound represented by the general
formula (I), (II), (III), (IV), (V) or (VI)

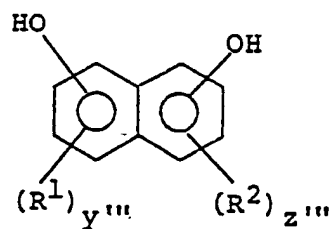




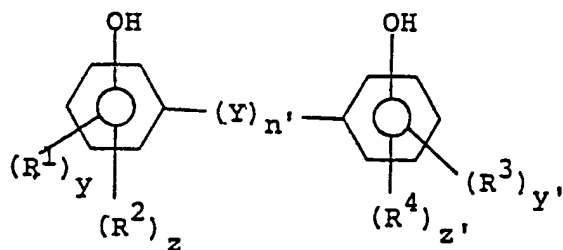
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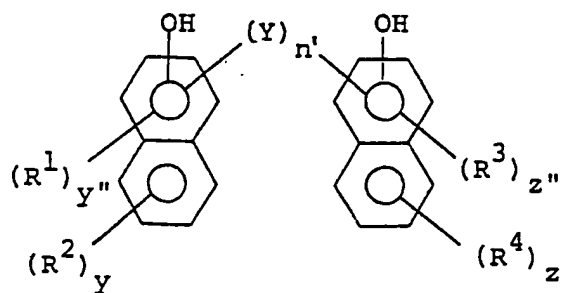
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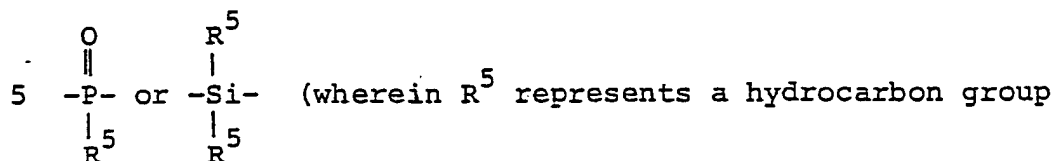
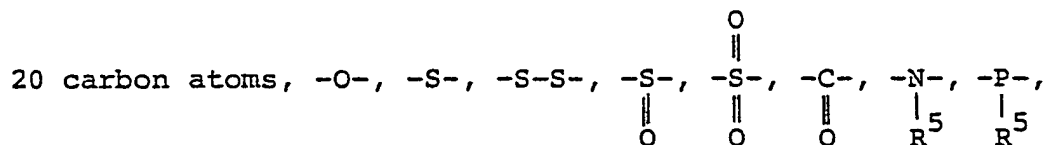


(V)



(VI)

- 1 which is used as the catalyst component (C) in the present invention, R" and R'" are each a hydrocarbon group of 1 to 20 carbon atoms, and Y is a hydrocarbon group of 1 to



- of 1 to 6 carbon atoms). As the hydrocarbon groups of 1 to 20 carbon atoms represented by R", R'" and Y, there can be mentioned, for example, groups such as methylene, ethylene, trimethylene, propylene, diphenylmethylene, ethylidene, n-propylidene, isopropylidene, n-butylidene and isobutylidene. Of these, methylene, ethylene, ethylidene, isopropylidene and isobutylidene groups are used preferably. n' is 0 or an integer of 1 or larger and represents the times of repetition of the unit Y.
- 15 Particularly, 0 or 1 gives a preferable result.

- R¹, R², R³ and R⁴ each represents a hydrocarbon group of 1 to 20 carbon atoms, a hydroxyl group, a nitro group, a nitrile group, a hydrocarbyloxy group of a halogen atom. As examples of the hydrocarbon group of 1 to 20 carbon atoms, there can be mentioned alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, n-amyl, isoamyl, n-hexyl, n-heptyl, n-octyl, n-decyl, n-dodecyl and the like; aryl groups such as phenylnaphthyl and the like; cycloalkyl groups

1 such as cyclohexyl, cyclopentyl and the like; allyl groups such as propenyl and the like; and aralkyl groups such as benzyl and the like. Of these, alkyl groups of 1 to 10 carbon atoms can be used preferably.

5 y, y', y'', y''', z, z', z'' and z''' each represents the number of a substituent bonding to an aromatic ring.

y, y', z and z' each represents 0 or an integer of 1 to 4;

y'' and z'' each represents 0 or an integer of 1 to 2;

and y''' and z''' each represents 0 or an integer of 1 to

10 3.

As specific examples of the catalyst component (C), there can be mentioned 2,4-dihydroxypentane, 2-(2-hydroxypropyl)phenol, catechol, resorcinol, 4-isopropylcatechol, 3-methoxycatechol, 1,8-dihydroxynaphthalene, 15 1,2-dihydroxynaphthalene, 2,2'-biphenyldiol, 1,1'-bi-2-naphthol, 2,2'-dihydroxy-6,6'-dimethylbiphenyl, 4,4',6,6'-tetra-t-butyl-2,2'-methylenediphenol, 4,4'-dimethyl-6,6'-di-t-butyl-2,2'-methylenediphenol, 4,4',6,6'-tetramethyl-2,2'-isobutylidenediphenol, 2,2'-dihydroxy-20 3,3'-di-t-butyl-5,5'-dimethyldiphenyl sulfide, etc. Of these, 2,4-dihydroxypentane, catechol, 2,2'-biphenyldiol, 1,1'-bi-2-naphthol, 4,4',6,6'-tetra-t-butyl-2,2'-methylenediphenol, 4,4'-dimethyl-6,6'-di-t-butyl-2,2'-methylenediphenol, 4,4',6,6'-tetramethyl-2,2'-25 isobutylidenediphenol and 2,2'-dihydroxy-3,3'-di-t-butyl-5,5'-dimethyldiphenyl sulfide give preferable results.

In application of these catalyst systems to

1 olefin polymerization, only the catalyst components (A)
and (B) or the catalyst components (A), (B) and (C) can
be used. In polymerization of, for example, propylene,
the use of the catalyst components (A) and (B) produces
5 mainly an atactic (amorphous) polymer of very high
molecular weight and no stereoregularity, while the use
of the catalyst components (A), (B) and (C) produces
a crystalline polymer of isotactic stereoregularity
depending upon the type of the catalyst component (C).

10 With respect to the addition amount of each
catalyst component, in the case of, for example, solvent
polymerization, the catalyst component (A) can be used
in a range of 10^{-10} to 10^3 mmol/l, preferably 10^{-7} to 10^2
mmol/l in terms of transition metal atom.

15 The catalyst component (B) can be used in a
ratio of aluminum atom to transition metal atom of the
catalyst component (A), of 1-100,000, preferably
10-10,000.

The catalyst component (C) can be used in a
20 mole ratio to transition metal atom of the catalyst
component (A), of 0.01-4.

It is necessary that the polymerization com-
ponent (C) is allowed to react, before its use in polymer-
ization, with the catalyst component (A). The reaction
25 can be effected at temperatures of -20° to 200°C in a
hydrocarbon or halogenated hydrocarbon solvent. The
catalyst component (C) can be directly reacted with
the catalyst component (A); however, when the catalyst

1 component (A) is a halogen-containing transition metal
compound, it is possible to add, to the reaction
system, ammonia, pyridine, an alkylamine or the like
in order to capture hydrogen halide which generates
5 during the reaction. In this case, it is preferable that
the reaction product is used in polymerization after
the hydrogen halide-containing compound precipitated
have been removed. It is also possible that the
catalyst component (C) is allowed to react with an alkali
10 metal (e.g. metallic sodium) or its hydride (e.g. lithium
hydride) to synthesize a metal alcoholate, a metal
phenolate, a metal naphtholate or the like and this
synthesized product is allowed to react with the
catalyst component (A). In this case, it is preferable
15 that the synthesized product is used in polymerization
after the alkali metal salt precipitated has been
removed. It is moreover possible that when the catalyst
component (A) contains hydrocarbyloxy group, the catalyst
component (C) is allowed to react with a carboxylic
20 acid (e.g. acetic acid) to obtain an ester compound and
this ester compound is subjected to reaction with the
catalyst component (A).

When a transition metal compound and an organic
compound having at least 2 hydroxyl groups are reacted,
25 the reaction product is believed to have a structure in
which the at least 2 hydroxyl groups of said organic
compound bonded to one transition metal atom.

The olefins to which the present invention can

1 be applied are those having 2 to 10 carbon atoms.
Specific examples of the olefins are ethylene, propylene,
butene-1, pentene-1, 4-methylpentene-1, hexene-1,
octene-1, vinylcyclohexane, etc. These compounds can be
5 subjected to homopolymerization as well as to copolymer-
ization of two or more olefins. The olefins usable
in the present invention should not be restricted to
those mentioned above.

The polymerization method should not be
10 restricted to a particular one, either. There can be
used, for example, solvent polymerization using a
aliphatic hydrocarbon solvent (e.g. butane, pentane,
hexane, heptane, octane), an aromatic hydrocarbon
solvent (e.g. benzene, toluene) or a halogenated
15 hydrocarbon solvent (e.g. methylene chloride); solution
polymerization; bulk polymerization using a monomer
(monomers) as a solvent; and gas phase polymerization
conducted in gaseous monomer(s). Any of continuous
polymerization and batch polymerization can be used.

20 The polymerization temperature can vary in a
range of -50° to 200°C . Particularly, a temperature
range of -20° to 100°C is preferred. As the polymeriza-
tion pressure, normal pressure to $60\text{ kg/cm}^2\text{G}$ is
preferred. The polymerization time is generally
25 determined appropriately depending upon the type
of polymer desired and the reactor used; however, it can
vary from 5 minutes to 40 hours. For example, 5 minutes
to 10 hours is preferred in ethylene polymerization and

1 30 minutes to 20 hours is preferred in propylene polymerization.

Example

Next, the effects of the present invention
5 will be explained specifically by way of Examples of the present invention and Comparative Examples. However, the present invention is in no way restricted by these Examples.

In the Examples each molecular weight was
10 shown as an intrinsic viscosity $[\eta]$ or as a weight-average molecular weight calculated using gel permeation chromatography (GPC).

The measurement of $[\eta]$ was conducted at 135°C for a tetralin solution.

15 In GPC, Model 150C, an apparatus manufactured by Waters was used. The measurement was conducted at 140°C using o-dichlorobenzene as a solvent. Three Shodex 80M/S columns were used. For preparation of a calibration curve, there were used 14 kinds of monodisperse
15 standard polystyrene whose molecular weights ranged from 500 to 6.8×10^6 . The molecular weight of each polymer obtained was shown as a weight-average molecular weight calculated from an average molecular weight in terms of styrene according to the Universal method.

20 The isotactic stereoregularity of polymer obtained in propylene polymerization was evaluated by

1 measuring the presence of isotactic crystalline band
at 997 cm^{-1} in the IR spectrum, or by using an isotactic
triad mole fraction (hereinafter referred to as [mm]
fraction) calculated from the ^{13}C NMR spectrum. The
5 measurement was conducted at 135°C using a FX-100
Spectrometer manufactured by Nihon Denshi. Incidentally,
the polymer sample was dissolved in o-dichlorobenzene.
The [mm] fraction was calculated from the enlarged
spectrum of the methyl carbon region.

10 Example 1

(1) Synthesis of methylaluminoxane [catalyst component
(C)]

A flask having an internal volume of 0.5 liter,
equipped with a stirrer, a dropping funnel and a reflux
15 condenser was purged with argon. Therein was placed 200
ml of toluene. Then, 38.2 g (0.15 mole) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was
added and suspended in the toluene. While the contents of
the flask was maintained at 25°C and stirred, a solution
consisting of 0.58 mole of trimethylaluminum and 100 ml
20 of toluene was added dropwise in 5 hours. After the
completion of the dropwise addition, stirring was
continued for 20 hours at room temperature. The precipi-
tate formed was removed, after which the solvent was
removed under vacuum to obtain 14.3 g of methylaluminoxane.
25 This aluminoxane was used in polymerization after dilution
with toluene (0.1 g/ml). The aluminoxane synthesized in
this Example was used also in Examples 2 to 5 and

1 Comparative Example 2.

(2) Polymerization of propylene

A stainless steel autoclave having an internal volume of 130 ml, of magnetic stirrer mixing type was
5 purged with argon. Thereinto were charged 500 μ l of a toluene solution containing tetra-n-butoxytitanium as a catalyst component (A) (the solution contained 8.62×10^{-6} mole of titanium), 3 ml of methylaluminoxane and 80 ml of liquefied propylene.

10 The autoclave was kept at 30°C for 1 hour with stirring. Excessive propylene was released out, after which the polymer formed was recovered.

The polymer was washed with 1 N HCl dissolved in methanol, followed by washing with methanol and
15 drying. The resulting polymer weighed 0.78 g, which corresponded to a catalyst activity of 9.4×10^4 g of polymer per mole of titanium atom. This polymer had an $[\eta]$ of 3.5 and was found from the IR spectrum to be an amorphous polypropylene.

20 Example 2

Polymerization was conducted in the same manner as in Example 1 except that 50 μ l of a tetra-n-butoxytitanium solution containing 8.62×10^{-7} mole of titanium was used as a catalyst component (A) and a polymerization
25 temperature of 60°C was employed. The resulting polymer weighed 0.32 g, which corresponded to a catalyst activity

- 1 of 3.7×10^5 g of polymer per mole of titanium atom.
This polymer had an $[\eta]$ of 2.2 and was found from the
IR spectrum to be an amorphous polypropylene.

Example 3

- 5 Polymerization was conducted in the same manner
as in Example 1 except that 5 ml of a tetra-n-butoxy-
titanium solution containing 8.62×10^{-5} mole of titanium
was used as a catalyst component (A) and a polymerization
time of 4 hours was employed. The resulting polymer
10 weighed 1.33 g. This polymer had an $[\eta]$ of 6.1 and was
found from the IR spectrum to be an amorphous polypropylene.

Example 4

- Polymerization was conducted in the same manner
15 as in Example 1 except that 500 μ l of a tetraisopropoxy-
titanium solution containing 1.01×10^{-5} mole of
titanium was used as a catalyst component (A) in place
of the tetra-n-butoxytitanium solution. The resulting
polymer weighed 2.3 g. This polymer had an $[\eta]$ of 2.5
20 and was found from the IR spectrum to be an amorphous
polypropylene.

Example 5

- Polymerization was conducted in the same manner
as in Example 1 except that 500 μ l of a diphenoxytitanium
25 dichloride solution containing 9.2×10^{-6} mole of titanium

1 was used as a catalyst component (A) in place of
tetra-n-butoxytitanium and a polymerization time of 4
hours was employed. The resulting polymer weighed 2.9 g.
This polymer had an $[\eta]$ of 2.1 and was found from the IR
5 spectrum to be an amorphous polypropylene.

Comparative Example 1

Polymerization was conducted in the same manner
as in Example 1 except that 18 ml of a toluene solution
of ethylaluminum sesquichloride (0.29 mmol/ml solution)
10 was used in place of methylaluminoxane as a catalyst
component (B). The resulting polymer weighed 2 mg.
Therefore, the catalyst system used had a low activity.

Comparative Example 2

Polymerization was conducted in the same
15 manner as in Example 1 except that 8.6×10^{-7} mole of
biscyclopentadienyltitanium dichloride was used in place
of tetra-n-butoxytitanium as a catalyst component (A).
The resulting polymer weighed 0.28 g. This polymer
had an $[\eta]$ of 0.03 and was a sticky amorphous polypro-
20 pylene.

Example 6

(1) Reaction of catalyst components (A) and (C)

A flask having an internal volume of 500 ml,
equipped with a stirrer, a dropping funnel and a reflux
25 condenser was purged with argon. 100 ml of methylene

1 chloride and 0.015 mole of titanium tetrachloride were
placed in the flask and they were heated until methylene
chloride was refluxed. Then, a solution consisting of
200 ml of methylene chloride and 0.015 mole of 1,1'-
5 bi-2-naphthol was dropped from the dropping funnel
slowly in 3 hours. After the completion of the dropping,
stirring was continued for 1 hour under refluxing. The
reaction mixture was allowed to stand overnight and
filtered to remove the precipitate formed, whereby
10 a uniform black solution was obtained. This solution
contained 0.04 mmole/ml of titanium.

(2) Synthesis of catalyst component (B)

A flask having an internal volume of 0.5 liter,
equipped with a stirrer, a dropping funnel and a reflux
15 condenser was purged with argon. 200 ml of toluene was
placed in the flask. Then, 38.2 g (0.15 mole) of
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was added and suspended in toluene. While the
content of the flask was maintained at 25°C and stirred, a
solution consisting of 0.58 mole of trimethylaluminum
20 and 100 ml of toluene was added dropwise in 5 hours.
After the completion of the dropwise addition, stirring
was continued for 20 hours at room temperature.

The precipitate was removed. Then, the solvent
was removed under vacuum to obtain 12.0 g of methyl-
25 aluminoxane. This methylaluminoxane was used in
polymerization after dilution with toluene (0.1 g/ml).
This aluminoxane solution was used also in polymerizations

1 of Examples 8 to 13 and Comparative Example 3.

(3) Polymerization of propylene

A stainless steel autoclave having an internal volume of 130 ml, of magnetic stirrer mixing type was
5 purged with argon. Thereinto were charged 0.1 ml of the reaction solution of the catalyst components (A) and (C) obtained in the above (1), 3 ml of the catalyst component (B) obtained in the above (2) and 80 ml of liquified propylene.

10 The autoclave was kept at 20°C for 1 hour with stirring. Excessive propylene was released out, after which the polymer formed was recovered.

The polymer was washed with 1 N HCl dissolved in methanol, followed by washing with methanol and
15 drying. The resulting polymer weighed 0.25 g, which corresponded to a catalyst activity of 62.5 g of polymer per mmole of titanium. This polymer had a molecular weight of 314,000 and a [mm] fraction of 0.55.

20 Example 7

In the synthesis of catalyst component (B) in Example 6, trimethylaluminum was replaced by triethylaluminum to synthesize ethylaluminoxane. Using a toluene solution of this ethylaluminoxane (0.1 g/ml) and
25 0.5 ml of the reaction solution of the catalyst components (A) and (C) obtained in Example 6, propylene polymerization

1 was conducted in the same manner as in Example 6. The resulting polymer weighed 146 mg. This polymer had a molecular weight of 274,000 and a $[\eta]$ fraction of 0.49.

Example 8

5 (1) Reaction of catalyst components (A) and (C)

A uniform black solution was obtained in the same manner as in the reaction of catalyst components (A) and (C) of Example 1 except that 0.015 mole of 2,2'-biphenyldiol was used in place of 1,1'-bi-2-naphthol.

10 This solution contained 0.027 mmole/ml of titanium.

(2) Polymerization of propylene

Polymerization was conducted in the same manner as in Example 6 except that 10 ml of the reaction solution
15 of catalyst components (A) and (C) and 9 ml of the same catalyst component (B) were used. The catalyst activity was 15.0 g of polymer per mmole of titanium. The polymer obtained had a molecular weight of 191,000 and a $[\eta]$ fraction of 0.50.

20 Example 9

A flask having an internal volume of 200 ml, equipped with a stirrer and a thermometer was purged with argon. Thereinto were charged 60 ml of methylene chloride, 20 ml of the reaction solution of catalyst components (A) and (C) obtained in Example 6 and 1.5 ml

1 of the catalyst component (B) obtained in Example 6.

The temperature inside the flask was maintained at 25°C; the inside gas of the flask was replaced by propylene; and the pressure inside the flask was kept
5 at 0.1 kg/cm²G. Under this condition, polymerization was conducted for 2 hours. The flask inside was purged again with argon; 1 N HCl dissolved in methanol was added; and stirring was continued for 0.5 hour. The toluene layer was evaporated to dryness to recover
10 1.9 g of a polymer. This polymer had a molecular weight of 258,000 and a [mm] fraction of 0.55.

Example 10

(1) Reaction of catalyst components (A) and (C)

A flask having an internal volume of 500 ml,
15 equipped with a stirrer; a dropping funnel and a reflux condenser was purged with argon. Therein were placed 100 ml of methylene chloride and 0.01 mole of zirconium tetrachloride. They were heated until methylene chloride refluxed.

20 Then, a solution consisting of 100 ml of toluene and 0.01 mole of 4,4',6,6'-tetra-t-butyl-2,2'-methylene-diphenol was dropped from the dropping funnel slowly in 2 hours. After the completion of the dropping, stirring was continued for 50 hours under refluxing.

25 The reaction mixture was allowed to stand overnight and then filtered to remove the resulting precipitate to obtain a uniform brown solution. This

1 solution contained 0.009 mmole/ml of zirconium.

(2) Polymerization of propylene

Polymerization was conducted in the same manner as in Example 6 except that 1 ml of the reaction solution of catalyst components (A) and (C) obtained in the above (1) was charged. The resulting polymer weighed 0.15 g and had a molecular weight of 309,000 and a [mm] fraction of 0.73.

Example 11

10 (1) Reaction of catalyst components (A) and (C)

A flask having an internal volume of 100 ml, equipped with a stirrer, a dropping funnel and a reflux condenser was purged with argon. Therein were placed 20 ml of methylene chloride and 0.0028 mole of 4,4',6,6'-tetramethyl-2,2'-isobutylidenediphenol. They were heated until methylene chloride was refluxed. Then, a methylene chloride solution containing 0.0028 mole of tetraisopropoxytitanium was dropped from the dropping funnel, and stirring was conducted for 1 hour under refluxing. The reaction mixture was subjected to vacuum to remove the solvent and then dried to obtain a reaction product. This reaction product was used in polymerization in a form of toluene solution (4.3×10^{-5} mole/ml).

(2) Polymerization of propylene

25 Polymerization was conducted in the same manner as in Example 6 except that 1 ml of the reaction solution

1 of catalyst components (A) and (C) obtained in the above
(1) was charged. The resulting polymer weighed 0.41 g
and had a molecular weight of 850,000 and a [mm]
fraction of 0.53.

5 Example 12

(1) Reaction of catalyst components (A) and (C)

Reaction was conducted in the same manner as
in Example 11 except that 0.0028 mmole of tetraisopropoxy-
zirconium was used as a catalyst component (A) in place
10 of tetraisopropoxytitanium, whereby a toluene solution
(4.0×10^{-5} mole/ml) was obtained.

(2) Polymerization of propylene

Polymerization was conducted in the same manner
as in Example 6 except that 1 ml of the reaction solution
15 of catalyst components (A) and (C) obtained in the above
(1) was used and the polymerization temperature and time
were 60°C and 4 hours, respectively. The resulting
polymer weighed 0.07 g and had a molecular weight of
730,000 and a [mm] fraction of 0.70.

20 Example 13

(1) Reaction of catalyst components (A) and (C)

Reaction was conducted in the same manner as
in Example 11 except that 0.0028 mmole of tetra-t-
butoxyzirconium was used as a catalyst component (A) in
25 place of tetraisopropoxytitanium, whereby a toluene

1 solution (6.0×10^{-5} mole/ml) was obtained.

(2) Polymerization of propylene

Polymerization was conducted in the same manner as in Example 6 except that 1 ml of the reaction solution
5 of catalyst components (A) and (C) obtained in the above (1) was used and the polymerization temperature and time were 80°C and 2 hours, respectively. The resulting polymer weighed 0.5 g. This polymer had a molecular weight of 500,000 and a $[\eta]$ fraction of 0.83.

10 Comparative Example 3

Polymerization was conducted in the same manner as in Example 6 except that 3 ml of a toluene solution containing biscyclopentadienyltitanium dichloride (1.2×10^{-5} mole/ml) was used as a catalyst component (A).

15 The resulting polymer weighed 3.6 g. This polymer had a low molecular weight of 2,800 and a $[\eta]$ fraction of 0.25 and was an amorphous polypropylene.

Comparative Example 4

Polymerization was conducted in the same manner
20 as in Example 9 except that 2.5×10^{-3} mole of diethylaluminum chloride was used as a catalyst component (C). Only a trace amount of a polymer was obtained.

Example 14

(1) Reaction of catalyst components (A) and (C)

1 A flask having an internal volume of 100 ml,
equipped with a stirrer and a reflux condenser was
purged with argon. Therein was placed 0.84 mmole of
2,2'-dihydroxy-3,3'-di-t-butyl-5,5'-dimethyldiphenyl
5 sulfide. Then, 50 ml of dry n-butyl ether was added.
They were stirred and made into a solution. To this
solution was slowly added an n-butyl ether solution
containing 0.84 mmole of titanium tetrachloride, using a
syringe. Stirring was conducted at 25°C for about 6
10 hours. After the reaction mixture had been allowed to
stand, the supernatant was removed to recover a precipi-
tate portion. Part of the precipitate was dissolved in
toluene to prepare a solution containing 0.001 mmole/ml
of titanium.

15 (2) Synthesis of catalyst component (B)

A flask having an internal volume of 500 ml,
equipped with a stirrer, a dropping funnel and a reflux
condenser was purged with argon. Therein was placed
200 ml of toluene. Then, 38.2 g (0.15 mole) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
20 was added and suspended in toluene. While the flask
contents was maintained at 5°C and stirred, a solution
consisting of 0.58 mole of trimethylaluminum and 100 ml
of toluene was dropped in 5 hours. After the completion
of the dropping, stirring was continued for 20 hours
25 at room temperature. The precipitate was removed and then
the solvent was removed under vacuum to obtain 10.0 g
of methylaluminoxane. This aluminoxane was used in

1 polymerization after dilution with toluene (0.05 g/ml).
The aluminoxane solution was used also in polymerization
of Examples 15 to 19 and Comparative Example 5.

(3) Polymerization of ethylene

5 In a 100-ml flask were placed 50 ml of toluene,
3 ml (150 mg) of the catalyst component (B) and 1 ml
(0.001 mmole) of the reaction solution of catalyst
components (A) and (C) in this order. The mixture was
heated to 30°C. Then, ethylene was continuously fed
10 into the flask and polymerization was conducted for 10
minutes at 0.2 kg/cm²G. After the completion of the
reaction, methanol was added to decompose the catalysts,
followed by drying to obtain 0.35 g of a polyethylene.
The catalyst activity was 2,100 g of polymer per mmole
15 of titanium per hour. The resulting polymer had a
molecular weight of 530,000.

Example 15

A stainless steel autoclave having an internal
volume of 130 ml, of magnetic stirrer mixing type was
20 purged with argon. Therein were placed the reaction
solution of catalyst components (A) and (C) (0.001 mmole)
and 3 ml of the catalyst component (B), both prepared in
Example 14, in this order. 40 g of propylene was fed
into the autoclave and polymerization was conducted
25 at 30°C for 1 hour. After the completion of the reaction,
propylene was purged and methanol was added to decompose

- 1 the catalysts, followed by drying to obtain 3.9 g of a polymer. This polypropylene had a molecular weight of 1,800,000.

Example 16

- 5 (1) Reaction of catalyst components (A) and (C)

In a flask having an internal volume of 100 ml, equipped with a stirrer was placed 0.9 mmole of 2,2'-dihydroxy-3,3'-di-t-butyl-5,5'-dimethyldiphenyl sulfide. The flask was purged with argon, after which 50 ml of dry n-butyl ether was added. The mixture was stirred and made into a solution. To this solution was added 0.9 mmole of tetraisopropoxytitanium. Stirring was conducted at 25°C and in few to several minutes, a precipitate appeared. Stirring was continued for about 15 2 hours and the mixture was allowed to stand. The supernatant was removed, and the precipitate portion was recovered and washed. A part of this precipitate was dissolved in toluene to prepare a solution containing 9.1×10^{-4} mmole/ml of titanium.

- 20 (2) Polymerization of propylene

Polymerization was conducted in the same manner as in Example 15 except that 1 ml of the reaction solution of catalyst components (A) and (C) obtained in the above (1) was added, whereby 0.86 g of a polymer was obtained. This polymer had a molecular weight of 1,600,000.

1 Comparative Example 5

(1) Polymerization of propylene

Polymerization was conducted in the same manner as in Example 15 except that 0.0009 mmole of biscyclopentadienylhafnium dichloride was used as a catalyst component (A) and further the catalyst component (B) obtained in Example 14 was used, whereby 0.8 g of a polymer was obtained. The polymer had a low molecular weight of 19,000.

10 Example 17

(1) Reaction of catalyst components (A) and (C)

A flask having an internal volume of 100 ml, equipped with a stirrer and a reflux condenser was purged with argon. Therein was placed 0.0053 mole of 2,4-dihydroxypentane. Thereto was added 30 ml of dry n-butyl ether. The mixture was stirred and made into a solution. To this solution was slowly added a n-butyl ether solution containing 0.0053 mole of titanium tetrachloride, using a syringe. Stirring was continued at 25°C for about 10 hours. The reaction mixture was allowed to stand. The supernatant was removed and the precipitate portion was recovered. A part of the precipitate was dissolved in toluene to prepare a solution containing 0.0023 mmole/ml of titanium.

25 (2) Polymerization of propylene

A stainless steel autoclave having an internal

1 volume of 130 ml, of magnetic stirrer mixing type was
purged with argon. Therein were placed the reaction
solution (0.0023 mmole) of catalyst components (A) and
(C) obtained in the above (1) and 3 ml of the catalyst
5 component (B) obtained in Example 14, in this order.
40 g of propylene was fed into the autoclave and poly-
merization was conducted at 30°C for 1 hour. After the
completion of the reaction, propylene was purged and
methanol was added to decompose the catalysts, followed
10 by drying to obtain 0.15 g of a polymer. The resulting
polypropylene had a molecular weight of 960,000 and was
found from the IR spectrum to be an amorphous polypro-
pylene.

Example 18

15 (1) Reaction of catalyst components (A) and (C)

A flask having an internal volume of 100 ml,
equipped with a stirrer and a reflux condenser was
purged with argon. Therein was placed 0.0053 mole of
catechol. Then, 30 ml of n-butyl ether was added, and
20 the mixture was stirred and made into a solution. To
this solution was slowly added a n-butyl ether solution
containing 0.0053 mole of titanium tetrachloride, using
a syringe. Stirring was conducted at 25°C for about
6 hours. The reaction mixture was evaporated to dryness.
25 A part of the residue was dissolved in toluene to prepare
a solution containing 0.18 mmole/ml of titanium.

1 (2) Polymerization of propylene

A stainless steel autoclave having an internal volume of 130 ml, of magnetic stirrer mixing type was purged with argon. Therein were placed the reaction
5 solution (0.18 mmole) obtained in the above (1) and 3 ml of the catalyst component (B) obtained in Example 14, in this order. Thereinto was fed 40 g of propylene and polymerization was conducted at 30°C for 1 hour. After the completion of the reaction, propylene was purged
10 and methanol was added to decompose the catalysts, followed by drying to obtain 0.02 g of a polymer. The resulting polypropylene had a molecular weight of 510,000 and was found from the IR spectrum to be an amorphous polypropylene.

15 Example 19

(1) Reaction of catalyst components (A) and (C)

A flask having an internal volume of 0.5 liter, equipped with a stirrer, a dropping funnel and a reflux condenser was purged with nitrogen. Therein
20 were placed 100 ml of methylene chloride and 0.015 mole of titanium tetrachloride. They were heated until methylene chloride were refluxed. Then, a solution consisting of 200 ml of methylene chloride and 0.015 mole of 1,1'-bi-2-naphthol was dropped from the dropping
25 funnel slowly in 1 hour. After the completion of the dropping, stirring was continued for 5 hours under refluxing. The reaction mixture was allowed to stand

1 overnight and then filtered to remove the precipitate
formed to obtain a uniform black solution. This solution
contained 0.04 mmole/ml of titanium.

(2) Synthesis of catalyst component (B).

5 A flask having an internal volume of 1 liter,
equipped with a stirrer, a dropping funnel and a reflux
condenser was purged with nitrogen. Therein was placed
400 ml of toluene. Then, 43.4 g (0.17 mole) of
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was added and suspended in toluene. While the
10 content of the flask was maintained at 5°C and stirred, a
solution consisting of 0.58 mole of trimethylaluminum
and 140 ml of toluene was dropped in 4 hours. Reaction
was conducted at this temperature for 1 hour and then
at 20°C for 24 hours. The reaction mixture was allowed
15 to stand over night. Subsequently, it was filtered
to remove the precipitate formed and the filtrate was
placed in vacuum to remove the solvent, whereby 11.3 g
of methylaluminoxane was obtained. This aluminoxane
was used in polymerization after dilution with toluene
20 (0.1 g/ml).

(3) Copolymerization of ethylene and propylene

A 0.5-liter flask equipped with a reflux
condenser was purged with argon. Therein were placed
200 ml of dry methylene chloride and 1 ml of the catalyst
25 component (B) obtained in the above (2). A thermometer
and a stirrer were attached to the flask, and the flask

- 1 inside temperature was kept at 30°C. A mixed gas
consisting of 50 mole % of ethylene and 50 mole % of
propylene was passed through the flask inside at a flow
rate of 3 liters (normal state)/minute for 10 minutes,
5 whereby the mixed gas was dissolved. Then, 1 ml of
the reaction solution of catalyst components (A) and (C)
obtained in the above (1) was added and copolymerization
was started. Polymerization was conducted for 1 hour
at 30°C with stirring while passing the above mixed gas.
10 The polymer solution was poured into a large amount of
methanol to recover a total amount of a copolymer. The
copolymer weighed 1.55 g. This copolymer contained 23%
by weight of propylene and had an $[\eta]$ of 8.4.

Example 20

- 15 (1) Copolymerization of ethylene and propylene
A 0.5-liter flask equipped with a reflux
condenser was purged with nitrogen. Therein were placed
200 ml of toluene and 1 ml of the catalyst component
(B) obtained in Example 19 (2). A thermometer and a
20 stirrer were attached to the flask, and the flask inside
temperature was kept at 50°C. A mixed gas consisting
of 40 mole % of ethylene and 60 mole % of propylene was
passed through the flask inside at a flow rate of 3 liters
(normal state)/minute for 10 minutes, whereby the mixed
25 gas was dissolved. Then, a toluene solution containing
0.017 mmole of tetraisopropoxytitanium was added as a
catalyst component (A), and copolymerization was started.

- 1 Polymerization was conducted for 1 hour at 50°C with stirring while passing the above mixed gas. The polymer solution was poured into a large amount of methanol to recover a total amount of a copolymer. The copolymer
- 5 weighed 0.34 g. This copolymer contained 25% by weight of propylene and had an $[\eta]$ of 8.8.

Industrial Applicability

- The process of the present invention enables production of high molecular olefin polymers at a high
- 10 efficiency. The present process has a very high industrial significance particularly in that high molecular amorphous olefin polymers whose production has hitherto been very difficult can be produced easily.

CLAIMS

1. A catalyst for olefin polymerization comprising:

a catalyst component (A) which is a transition metal compound represented by the general formula

$M(R)_l(OR')_mX_{n-(l+m)}$ (wherein M represents a transition metal atom; R and R' each represents a hydrocarbon group of 1 to 20 carbon atoms; X represents a halogen atom; l, m and n represent numbers satisfying $l \geq 0$, $m > 0$ and $n-(l+m) \geq 0$; and n corresponds to the valency of the transition metal), and

a catalyst component (B) which is an aluminoxane obtained by the reaction of a trialkylaluminum and water.

2. A catalyst for olefin polymerization comprising:

a catalyst component (A) which is a transition metal compound represented by the general formula

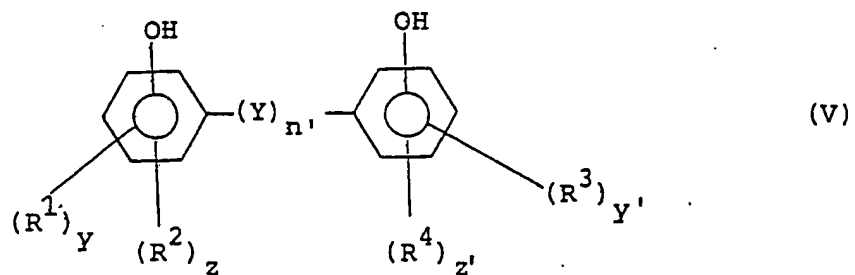
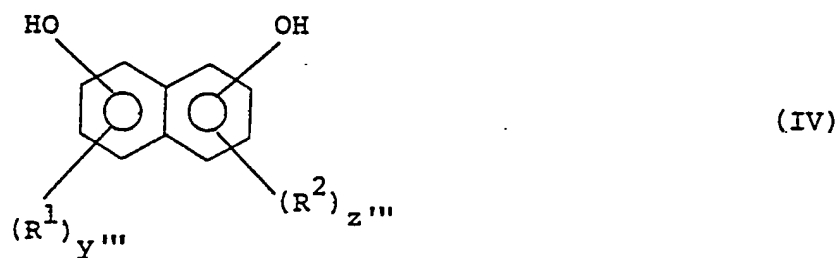
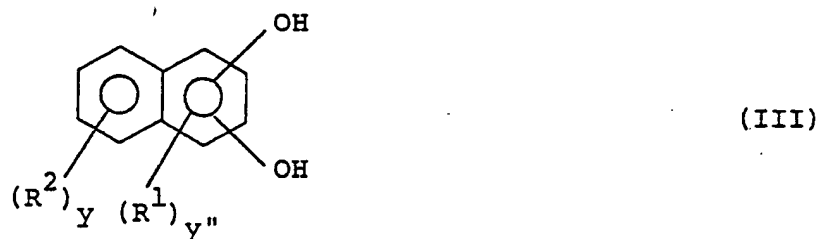
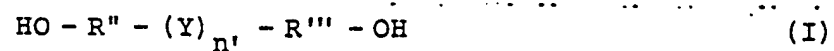
$M(R)_l(OR')_mX_{n-(l+m)}$ (wherein M represents a transition metal atom; R and R' each represents a hydrocarbon group of 1 to 20 carbon atoms; X represents a halogen atom; l, m and n represent numbers satisfying $l \geq 0$, $m \geq 0$ and $n-(l+m) \geq 0$; and n corresponds to the valency of the transition metal),

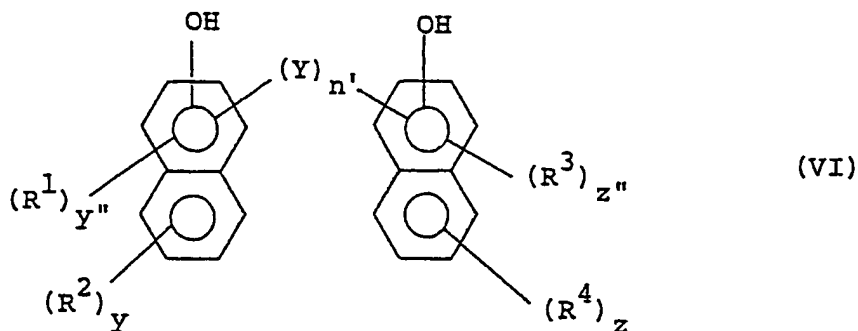
a catalyst component (B) which is an aluminoxane obtained by the reaction of a trialkylaluminum and water, and

a catalyst component (C) which is an organic compound having at least 2 hydroxyl groups, represented by the general formula (I), (II), (III), (IV), (V) or (VI)

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[wherein R" and R'" each represents a hydrocarbon group of 1 to 20 carbon atoms; Y represents a hydrocarbon

group of 1 to 20 carbon atoms, -O-, -S-, -S-S-, -S-, $\begin{array}{c} \text{O} \\ \parallel \\ \text{S-} \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ \text{S-} \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ \text{C-} \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ \text{N-} \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ \text{P-} \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ \text{P-} \end{array}$ or $\begin{array}{c} \text{R}^5 \\ | \\ \text{Si-} \\ | \\ \text{R}^5 \end{array}$ (wherein R⁵ represents

hydrogen or a hydrocarbon group of 1 to 6 carbon atoms); R¹, R², R³ and R⁴ each represents a hydrocarbon group of 1 to 20 carbon atoms, a hydroxyl group, a nitro group, a nitrile group, a hydrocarbyloxy group or a halogen atom, and R¹, R², R³ and R⁴ may be same or different; n' is 0 or an integer of 1 or larger and represents the times of repetition of the unit Y; y, y', y'', y''', z, z', z'' and z''' each represents the number of a substituent bonding to an aromatic ring, y, y', z and z' each represents 0 or an integer of 1 to 4, y'' and z'' each represents 0 or an integer of 1 to 2, and y''' and z''' each represents 0 or an integer of 1 to 3].

3. A catalyst for olefin polymerization according to Claim 1 or 2, wherein in the catalyst component (A),

the M of the transition metal compound represented by the general formula $M(R)_l(OR')_mX_{n-(l+m)}$ is titanium or zirconium.

4. A catalyst for olefin polymerization according to Claim 1 or 2, wherein in the catalyst component (A), the M of the transition metal compound represented by the general formula $M(R)_l(OR')_mX_{n-(l+m)}$ is titanium or zirconium, $l = 0$, $m > 0$ and $n-m \geq 0$.

5. A catalyst for olefin polymerization according to Claim 2, wherein in the catalyst component (A), the general formula $M(R)_l(OR')_mX_{n-(l+m)}$ is titanium tetrachloride or zirconium tetrachloride.

6. A catalyst for olefin polymerization according to Claim 1 or 2, wherein in the catalyst component (A), the R and R' of the general formula $M(R)_l(OR')_mX_{n-(l+m)}$ are each an alkyl group or an aryl group.

7. A catalyst for olefin polymerization according to Claim 1 or 2, wherein in the catalyst component (A), the R is a methyl, ethyl, phenyl or benzyl group and the R' is an n-propyl, isopropyl, n-butyl, t-butyl or a phenyl group.

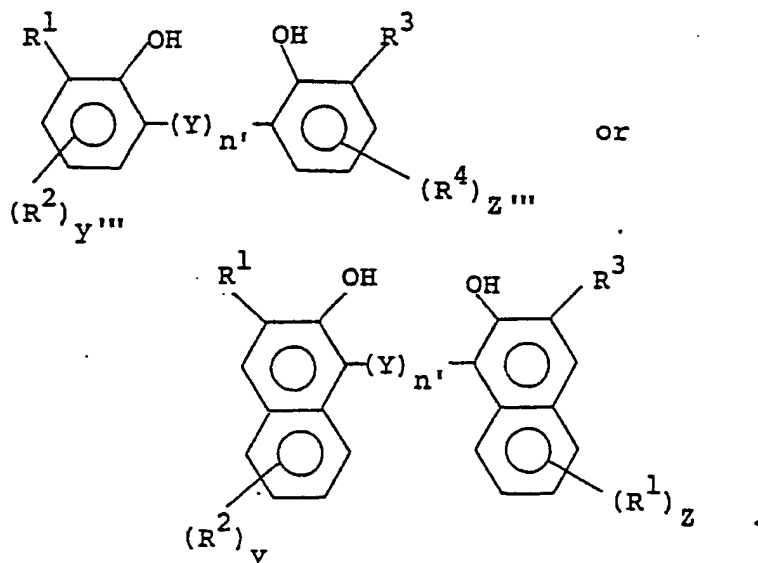
8. A catalyst for olefin polymerization according to Claim 1 or 2, wherein in the catalyst component (A), the general formula $M(R)_l(OR')_mX_{n-(l+m)}$ is tetraisopropoxytitanium, tetra-n-butoxytitanium, tetra-t-butoxytitanium, diphenoxytitanium dichloride, dinaphthoxytitanium dichloride, tetraisopropoxyzirconium, tetra-n-butoxyzirconium or tetra-t-butoxyzirconium.

9. A catalyst for olefin polymerization according to Claim 1, 2, 3, 4, 5, 6, 7 or 8, wherein in the catalyst component (B), the trialkylaluminum is trimethylaluminum or triethylaluminum.

10. A catalyst for olefin polymerization according to Claim 2, 3, 4, 5, 6, 7, 8 or 9, wherein the catalyst component (C) is a compound represented by the general formula (I) or (II).

11. A catalyst for olefin polymerization according to Claim 2, 3, 4, 5, 6, 7, 8 or 9, wherein the catalyst component (C) is a compound represented by the general formula (V) or (VI).

12. A catalyst for olefin polymerization according to Claim 11, wherein the catalyst component (C) is a compound represented by the general formula

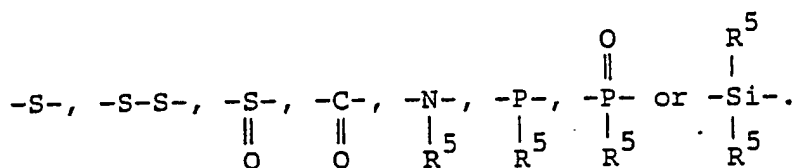


13. A catalyst for olefin polymerization according to Claim 12, wherein the catalyst component (C) is a compound in which the y , y''' , z and z''' are 1, respectively.

14. A catalyst for olefin polymerization according to Claim 11, 12 or 13, wherein the catalyst component (C) is a compound in which the n' is 1 and the Y is a hydrocarbon group of 1 to 20 carbon atoms.

15. A catalyst for olefin polymerization according to Claim 11, 12 or 13, wherein the catalyst component (C) is a biphenyldiol or binaphthol compound in which the n' is 0.

16. A catalyst for olefin polymerization according to Claim 11, 12 or 13, wherein the catalyst component (C) is a compound in which the n' is 1 and the Y is -O-,



17. A catalyst for olefin polymerization according to Claim 16, wherein the catalyst component (C) is a compound in which the n' is 1 and the Y is -S-.

18. A catalyst for olefin polymerization according to Claim 10, wherein in the catalyst component (C), the R'' and R''' are each a methylene, ethylene, ethylidene or isobutylidene group.

19. A catalyst for olefin polymerization according to Claim 10 or 11, wherein in the catalyst component (C), the R^1 , R^2 , R^3 and R^4 are each an alkyl group of 1 to 10 carbon atoms or an aryl group.

20. A catalyst for olefin polymerization according to Claim 19, wherein in the catalyst component (C), the R^1 , R^2 , R^3 and R^4 are each a methyl, ethyl, n-propyl,

isopropyl, n-butyl, isobutyl or t-butyl group.

21. A catalyst for olefin polymerization according to Claim 10, wherein the catalyst component (C) is 2,4-dihydroxypentane or catechol.

22. A catalyst for olefin polymerization according to Claim 15, wherein the catalyst component (C) is 2,2'-biphenyldiol or 1,1'-bi-2-naphthol.

23. A catalyst for olefin polymerization according to Claim 14, wherein the catalyst component (C) is 4,4',6',6'-tetra-t-butyl-2,2'-methylenediphenol, 4,4',6,6'-di-t-butyl-2,2'-methylenediphenol or 4,4',6,6'-tetramethyl-2,2'-isobutylidenediphenol.

24. A catalyst for olefin polymerization according to Claim 17, wherein the catalyst component (C) is 2,2'-dihydroxy-3,3'-di-t-butyl-5,5'-dimethyldiphenyl sulfide.

25. A process for producing an olefin polymer, characterized by homopolymerizing an olefin of 2 or more carbon atoms or copolymerizing two or more olefins of 2 or more carbon atoms, in the presence of a catalyst for olefin polymerization comprising:

a catalyst component (A) which is a transition metal compound represented by the general formula

$M(R)_l(OR')_mX_{n-(l+m)}$ (wherein M represents a transition metal atom; R and R' each represents a hydrocarbon group of 1 to 20 carbon atoms; X represents a halogen atom; l, m and n represent numbers satisfying $l \geq 0$, $m > 0$ and $n-(l+m) \geq 0$; and n corresponds to the valency of the

transition metal), and

a catalyst component (B) which is an aluminoxane obtained by the reaction of a trialkylaluminum and water.

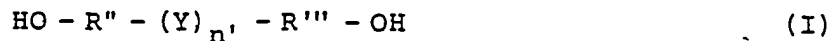
26. A process for producing an olefin polymer, characterized by homopolymerizing an olefin of 2 or more carbon atoms or copolymerizing two or more olefins of 2 or more carbon atoms, in the presence of a catalyst for olefin polymerization comprising:

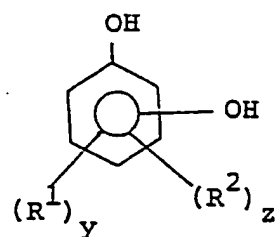
a catalyst component (A) which is a transition metal compound represented by the general formula

$M(R)_l(OR')_mX_{n-(l+m)}$ (wherein M represents a transition metal atom; R and R' each represents a hydrocarbon group of 1 to 20 carbon atoms; X represents a halogen atom; l, m and n represent numbers satisfying $l \geq 0$, $m \geq 0$ and $n-(l+m) \geq 0$; and n corresponds to the valency of the transition metal),

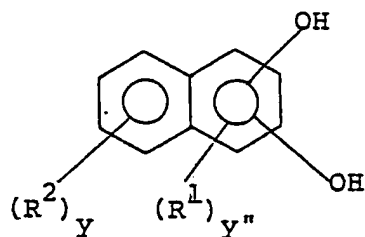
a catalyst component (B) which is an aluminoxane obtained by the reaction of a trialkylaluminum and water, and

a catalyst component (C) which is an organic compound having at least 2 hydroxyl groups, represented by the general formula (I), (II), (III), (IV), (V) or (VI)

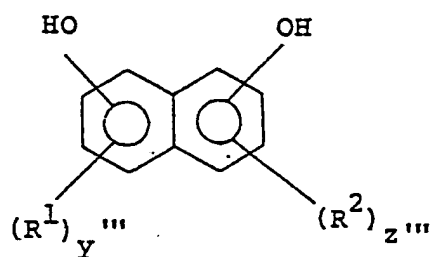




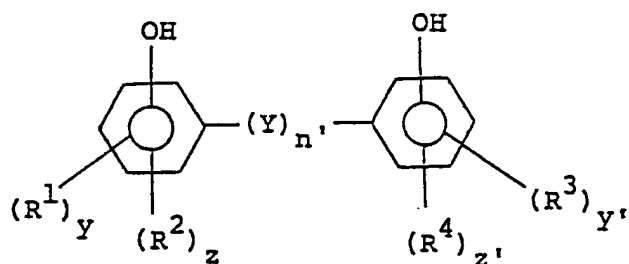
(II)



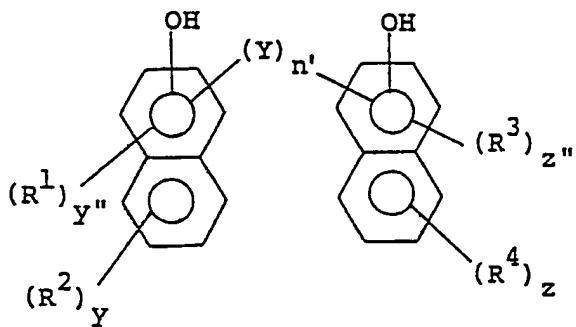
(III)



(IV)



(V)



(VI)

[wherein R" and R''' each represents a hydrocarbon group of 1 to 20 carbon atoms; Y represents a hydrocarbon group

of 1 to 20 carbon atoms, -O-, -S-, -S-S-, $\text{-}\overset{\text{O}}{\underset{\text{O}}{\text{S}}}\text{-}$, $\text{-}\overset{\text{O}}{\underset{\text{O}}{\text{S}}}\text{-}$,

$\text{-}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{-}$, $\text{-}\overset{\text{O}}{\underset{\text{R}^5}{\text{N}}}\text{-}$, $\text{-}\overset{\text{O}}{\underset{\text{R}^5}{\text{P}}}\text{-}$, $\text{-}\overset{\text{O}}{\underset{\text{R}^5}{\text{P}}}\text{-}$ or $\text{-}\overset{\text{R}^5}{\underset{\text{R}^5}{\text{Si}}}\text{-}$ (wherein R⁵ represents

hydrogen or a hydrocarbon group of 1 to 6 carbon atoms); R¹, R², R³ and R⁴ each represents a hydrocarbon group of 1 to 20 carbon atoms, a hydroxyl group, a nitro group, a nitrile group, a hydrocarboxyl group or a halogen atom, and R¹, R², R³ and R⁴ may be same or different; n' is 0 or an integer of 1 or larger and represents the times of repetition of the unit Y; y, y', y'', y''', z, z', z'' and z''' each represents the number of a substituent bonding to an aromatic ring, y, y', z and z' each represents 0 or an integer of 1 to 4, y'' and z'' each represents 0 or an integer of 1 to 2, and y''' and z''' each represents 0 or an integer of 1 to 3].

27. A process according to Claim 25 or 26, wherein in the catalyst component (A), the M of the transition metal compound represented by the general formula

$\text{M(R)}_l(\text{OR}')_m\text{X}_{n-(l+m)}$ is titanium or zirconium.

28. A process according to Claim 25, 26 or 27, wherein in the catalyst component (B), the trialkylaluminum is trimethylaluminum or triethylaluminum.

29. A process according to Claim 25, 26, 27 or 28,

wherein the catalyst component (C) is a compound represented by the general formula (I), (II), (V) or (VI).

30. A process according to Claim 25, 26, 27, 28 or 29, wherein the olefin(s) is (are) at least one olefin selected from ethylene, propylene, butene-1, pentene-1, 4-methylpentene-1, hexene-1, octene-1 and vinylcyclohexane.

INTERNATIONAL SEARCH REPORT

0241560

International Application No.

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl ⁴ C08F10/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁵		
Classification System	Classification Symbols	
IPC	C08F10/00, C08F10/02, C08F210/00, C08F4/64, C08F4/00	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁶		
Jitsuyo Shinan Koho 1947 - 1985 Kokai Jitsuyo Shinan Koho 1973 - 1985		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹¹		
Category ⁷	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	JP, A, 58-19309 (Hoechst A.G.) 4 February 1983 (04. 02. 83) (Family: none)	1-30
Y	JP, A, 60-35005 (Atkem) 22 February 1985 (22. 02. 85) (Family: none)	1-30
Y	JP, A, 58-65708 (Société Chimique des charbonnages S.A. 19 April 1983 (19. 04. 83) & FR, A1, 2509735, & EP, A1, 70749, & AU, A1, 8617782, & FR, B1, 2509735, & US, A, 4465781, & CA, A1, 1175799	1-30
<p>⁸ Special categories of cited documents: ¹⁹</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²		Date of Mailing of this International Search Report ²
December 16, 1986 (16.12.86)		January 12, 1987 (12.01.87)
International Searching Authority ¹		Signature of Authorized Officer ²⁰
Japanese Patent Office		